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ORGANIC PEROXIDES
A TABLE OF PHYSICAL CONSTANTS

- - - by - - -

Robert B. Mesrobian

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ORGANIC PEROXIDES: A Table of Physical Constants

- - - by - - -

Robert B. Mesrobian

Institute of Polymer Research, Polytechnic Institute of Brooklyn

During the past seventy years a wide variety of organic peroxides have been prepared. In the succeeding table, the physical constants of a selected number of peroxides are presented with reference to the original literature or to review articles which list the original references. For more general reference to the chemistry of organic peroxides, consult the articles of Rieche[1,2], Hawkins[3], Criegee[4] and others[5-8].

1. A. Riecho, Alkyl Peroxyde und Ozonyde, Steinkoff, Dresden, 1931.
2. A. Riecho, Die Bedeutung der Organischen Peroxyde fur die Chemische Wissenschaft u. Technik, Sammlung 34, 1936.
3. E.G.E.Hawkins, Quart. Reviews 4, 251 (1950).
4. R. Criegee, Fortschs. Chem. Forsch. 1, 508 (1950).
5. D. Swern, Chemical Reviews 45, 1 (1949).
6. J. E. Lefflor, ibid., 45, 385 (1949).
7. C. E. Frank, ibid., 46, 155 (1950).
8. D. Swern, J.T.Scanlon and H.B.Knight, J. Am. Oil Chemists' Soc., 25, 193 (1948).

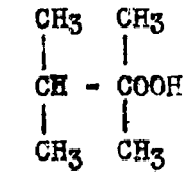
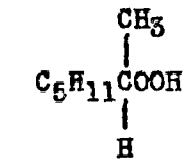
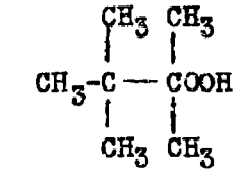
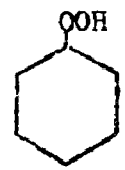
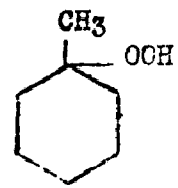
CONTENTS

1. PEROXIDES OF STRUCTURE ROOH (HYDROPEROXIDES)

Name	Formula	Refractivity $n_D^{20°}$	Melting Point °C.	Boiling Point °C/mm.Hg.	Literature Reference**
A. Saturated Aliphatic Hydroperoxides					
Methyl Hydroperoxide	CH_3OOH	1.3608	-72 to -78	log p= 8.38-1972/T.°K.	1,2
Ethyl Hydroperoxide	C_2H_5OOH	1.3801	glass @ -100	log p= 8.834-2228/T.°K.	1,2,3,4,5
Propyl Hydroperoxide	C_3H_7OOH	n_D^{25}=1.3890	glass @ -90	35/20	4,6
isoPropyl Hydroperoxide	$(CH_3)_2CHOOH$	n_D^{23}=1.8861	———	107 to 109/760	5,6
tert-Butyl Hydroperoxide*	$(CH_3)_3COOH$	1.4007	-8 to -10	log p= 8.891-2342/T.°K.	2,5,7,8,9 10,11
tert-Amyl Hydroperoxide	$C_2H_5(CH_3)_2COOH$	1.4161	———	26/3	5,12
Triethylmethyl Hydroperoxide	$(CH_3CH_2)_3COOH$	1.4379	2 to 3	27.5 to 28/2	9.10,13

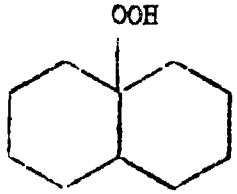
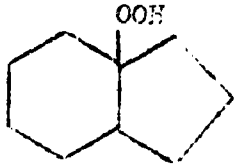
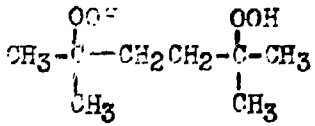
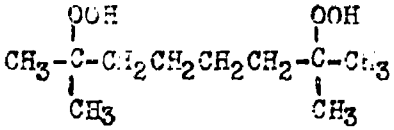
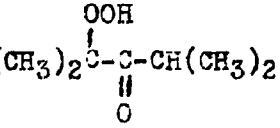
*These peroxides have been prepared by oxidation of the corresponding hydrocarbon with molecular oxygen.

**The physical constants are taken from the underlined reference.

Name	Formula	Refractivity $n_D^{20°}$	Melting Point °C.	Boiling Point °C/mm.Hg.	Literature Reference**
1,1,2,2-Tetramethylethyl Hydroperoxide		———	———	51 to 58/12	10
Amylmethylmethyl Hydroperoxide		1.4305	———	58/0.08	14
Pentamethylethyl Hydroperoxide		———	113 to 114	———	10, 13
Cyclohexyl* Hydroperoxide		n_D^{25}=1.4638	-20	———	15
1-Methylcyclohexyl Hydroperoxide-1*		1.4642	———	53/0.1	10, 16, 17

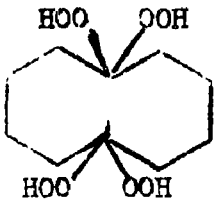
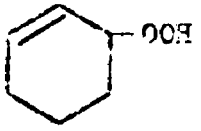
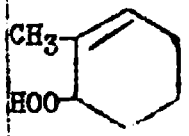
*These peroxides have been prepared by oxidation of the corresponding hydrocarbon with molecular oxygen.

**The physical constants are taken from the underlined reference.

Name	Formula	Refractivity $n_D^{20°}$	Melting Point °C.	Boiling Point °C/mm.Hg.	Literature Reference**
transDecalin* Hydroperoxide-9		———	94 to 95	———	10
transHydrindane* Hydroperoxide-8		———	———	73 to 75/0.2	18
2,5-Dihydroperoxy-2,5-dimethylhexane*		———	106.5	———	10,19
2,7-Dihydroperoxy-2,7-dimethyloctane		———	66	———	10
2-(2,4-Dimethyl-pentanone-3-yl)* hydroperoxide		1.4321	———	62 to 69/0.8	107

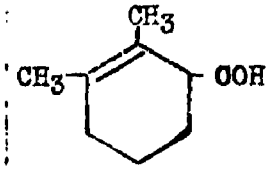
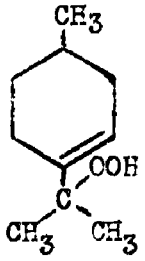
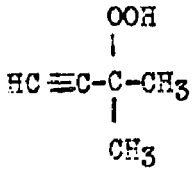
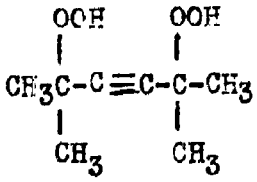
*These peroxides have been prepared by oxidation of the corresponding hydrocarbon with molecular oxygen.

** The physical constants are taken from the underlined reference.

Name	Formula	Refractivity $n_D^{20°}$	Melting Point °C.	Boiling Point °C/mm.Hg.	Literature Reference**
9,9,10,10-Tetrahydro-peroxycyclodecane		——	116 to 118	——	10
B. Olefin Hydroperoxides					
Cyclopentene-1-* hydroperoxide-3	 (not isolated in highest purity)	——	——	35/0.01	20
Cyclohexene-1* hydroperoxide-3	 (not isolated in highest purity)	n_D=30.75	——	51/0.3	20,21
1-Methylcyclohexene-* 1-hydroperoxide-6	 (not isolated in highest purity)	——	——	64 to 67/0.2	20,21,22

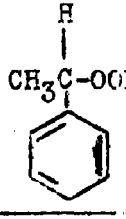
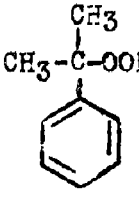
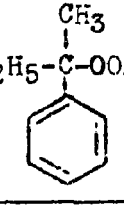
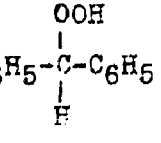
*These peroxides have been prepared by oxidation of the corresponding hydrocarbon with molecular oxygen.

**The physical constants are taken from the underlined reference.

Name	Formula	Refractivity $n_D^{20°}$	Melting Point °C.	Boiling Point °C/mm.Hg.	Literature Reference**
1,2-Dimethylcyclohexene-3-1-hydroperoxide*		———	———	67 to 70/0.5	19,20
d,l-3-p-Menthenyl Hydroperoxide*		1.47812	———	57.5/0.05	23
3-Methyl-3-hydroperoxy-butyne-1		n_D^{25}=1.4295	———	42 to 42.2/17	24
2,5-Dimethyl-2,5-dihydro-peroxyhexyne-3		———	107 to 109 (dec.)	———	24

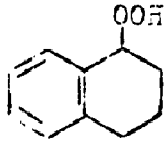
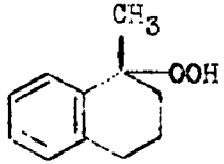
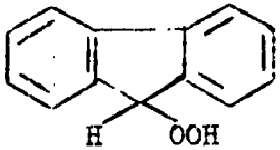
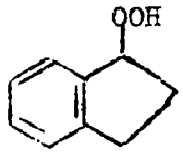
*These peroxides have been prepared by oxidation of the corresponding hydrocarbon with molecular oxygen.

**The physical constants are taken from the underlined reference.

Name	Formula	Refractivity $n_D^{20°}$	Melting Point °C.	Boiling Point °C/mm.Hg.	Literature Reference**
		C. Aralkyl Hydroperoxides			
Phenylmethylmethyl* Hydroperoxide		1.52695	———	45/0.05	25
Phenyldimethylmethyl* Hydroperoxide (cumene hydroperoxide)		1.5237	———	65/0.18	26,27,28,106
Phenylmethylethyl-* methyl hydroperoxide		1.5208	———	48 to 49/0.002	29,30
Diphenylmethyl* hydroperoxide		———	51	———	27
Triphenylmethyl* Hydroperoxide	$(C_6H_5)_3C\text{-}OOH$	———	82	———	31,32,33

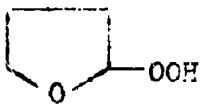
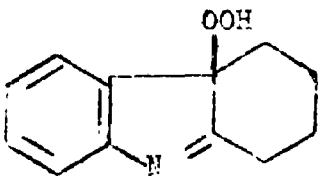
*These peroxides have been prepared by oxidation of the corresponding hydrocarbon with molecular oxygen.

**The physical constants are taken from the underlined reference.

Name	Formula	Refractivity $n_D^{20°}$	Melting Point °C.	Boiling Point °C/mm.Hg.	Literature Reference**
1,2,3,4-Tetrahydronaphthalene Hydroperoxide-1* (Tetralin Hydroperoxide)		$n_{He}^{78.7}$=1.54471	56	———	34,35
1-Methyl-1,2,3,4-tetrahydronaphthalene* Hydroperoxide-1		———	——	99 to 100/0.01	31
9-Fluoranyl Hydroperoxide*		———	93	———	36
1-Hydrindene Hydroperoxide*		1.56214	——	64 to 65/0.01	37

*These peroxides have been prepared by oxidation of the corresponding hydrocarbon with molecular oxygen.

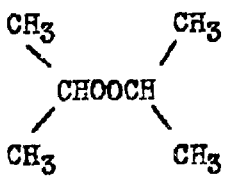
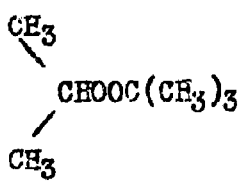
**The physical constants are taken from the underlined reference.

Name	Formula	Refractivity $n_D^{20°}$	Melting Point °C.	Boiling Point °C/mm.Hg.	Literature Reference**
		D. Hydroperoxides of Heterocyclic Compounds			
Tetrahydrofuryl Hydroperoxide*		1.6933	——	——	38
Tetrahydrocarbazole Hydroperoxide*	 (structure not proven)	——	123 to 124	——	39
Hydroperoxides having the structure, $R_1N{=}N{-}\overset{\overset{OOH}{|}}{C}{-}R_2$ (with R_3 below), prepared by autoxidation of the hydrazones of ketones and aldehydes and where R_1, R_2, R_3 are hydrogen, alkyl or aryl groups.					40

*These peroxides have been prepared by oxidation of the corresponding hydrocarbon with molecular oxygen.

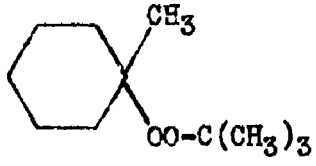
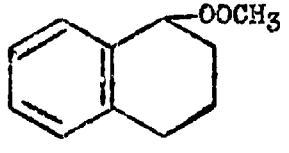
**The physical constants are taken from the underlined reference.

2. PEROXIDES OF STRUCTURE ROOR (DIALKYL PEROXIDES)

Name	Formula	Refractivity $n_D^{20°}$	Melting Point °C.	Boiling Point °C/mm.Hg.	Literature Reference**
		A. Dialkyl Peroxides			
Dimethyl Peroxide	CH_3OCCH_3	1.35029	-100 to -105	13.5/740	41, 42, 43
Methylethyl Peroxide	$CH_3OOC_2H_5$	1.3698	-68 to -69.5	log p= 7.356-1517/T°K.	2, 43
Diethyl Peroxide	$C_2H_5OOC_2H_5$	1.37156	———	64/740	41, 43, 44
Dipropyl Peroxide	$C_3H_7OOC_3H_7$	$n_D^{20.5}$=1.3911	———	———	3, 4, 41, 43
Diisopropyl Peroxide		———	———	53 to 54/760	45
Methyltertbutyl Peroxide	$CH_3OOC(CH_3)_3$	1.3761	-102.1	23/119	46
Ethyltertbutyl Peroxide	$C_2H_5OOC(CH_3)_3$	1.3840	-83.1	35/84	46
isoPropyltertbutyl Peroxide		1.3860	glass	52/125	46

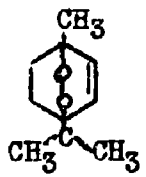
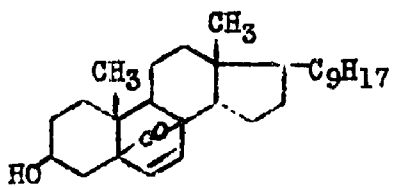
*These peroxides have been prepared by oxidation of the corresponding hydrocarbon with molecular oxygen.

**The physical constants are taken from the underlined reference.

Name	Formula	Refractivity $n_D^{20°}$	Melting Point °C.	Boiling Point °C/mm.Hg.	Literature Reference**
n-Butyltertbutyl Peroxide	$n\text{-}C_4H_9OOC(CH_3)_3$	1.4001	glass	53/30	46
sec-Butyltertbutyl Peroxide	$sec.C_4H_9\cdot OOC(CH_3)_3$	1.3959	-67.7	53/50	46
Di-tertbutyl Peroxide*	$(CH_3)_3C\cdot OOC(CH_3)_3$	1.3890	-40.0	111/760	46
tert-Butyltertamyl Peroxide*	$(CH_3)_3COOC(CH_3)_3C_2H_5$	1.4000	——	91 to 92/760	47
Di-tertamyl Peroxide*	$C_2H_5(CH_3)_2COOC(CH_3)_2C_2H_5$	1.4091	——	58.5/14	11, 47
tert-Butyl-1-methyl-cyclohexyl-1-Peroxide		1.4350	——	28 to 29/2.5	13
Tetrahydronaphthyl-methyl Peroxide		1.53406	——	72.5/0.03	23

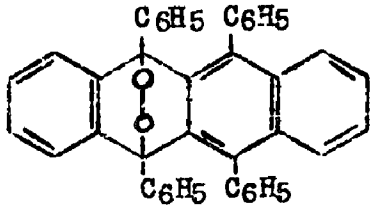
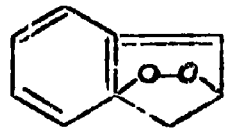
*These peroxides have been prepared by oxidation of the corresponding hydrocarbon with molecular oxygen.

**The physical constants are taken from the underlined reference.

Name	Formula	Refractivity $n_D^{20°}$	Melting Point °C.	Boiling Point °C/mm.Hg.	Literature Reference**
		B. Hexarylethane Peroxides			
Di-triphenylmethyl Peroxide*	$(C_6H_5)_3COOC(C_6H_5)_3$	———	185 to 186	———	48
A wide variety of other hexaarylethane peroxides have been prepared by the oxidation of symmetrical or unsymmetrical hexaarylethanes; consult, for example, reference (49).					
		C. Transannular Peroxides			
Ascaridole		n_D^{25}= 1.4769	———	96 to 97/8	50, 51, 52
Ergosterol Peroxide*	(Most probable structure) 	———	178	———	53, 54
Anthracene Peroxide*		———	120 (Decomposes)	———	54, 55

*These peroxides have been prepared by oxidation of the corresponding hydrocarbon with molecular oxygen.

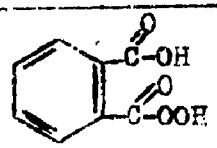
**The physical constants are taken from the underlined reference.

Name	Formula	Refractivity $n_D^{20°}$	Melting Point °C.	Boiling Point °C/mm.Hg.	Literature Reference**
Rubrene Peroxide*		——	Starts to lose oxygen at 100°C.	——	54,56
Cyclohexadiene Peroxide*		$n_D^{85°}$=1.453	82 to 83	40 to 55/0.3	50
2,8-endo-Peroxy-isoindene*		n_D^{22}=1.566	16 to 18	80/0.1	36,50

*These peroxides have been prepared by oxidation of the corresponding hydrocarbon with molecular oxygen.

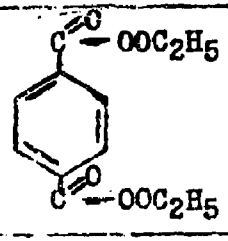
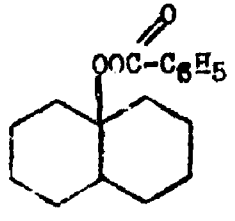
** The physical constants are taken from the underlined reference.

3. PEROXIDES OF STRUCTURE $RC(=O) - OOH$ (PERACIDS)

Name	Formula	Refractivity $n_D^{20°}$	Melting Point °C.	Boiling Point °C/mm.Hg.	Literature Reference**
A. Aliphatic Peracids					
Performic Acid*	$HC(=O) - OOH$ (not isolated in pure form)	——	——	——	57,58
Peracetic Acid*	$CH_3C(=O) - OOH$	——	0.1	20 to 30/10 to 20	59,60,61, 62
Perpropionic Acid*	$C_2H_5C(=O) - OOH$	——	-13.5	——	59,61,62, 63
Percaproic Acid	$C_4H_9C(=O) - OOH$	——	15	61 to 62/13	64
Permonochloracetic Acid	$CH_2ClC(=O) - OOH$	——	——	33 to 34 (decomp.)	65,66
B. Aromatic Peracids					
Perbenzoic Acid*	$C_6H_5C(=O) - OOH$	——	41	97 to 110/13 to 15	62,67
Monoperphthalic Acid		——	110 (decomp.)	——	62,67

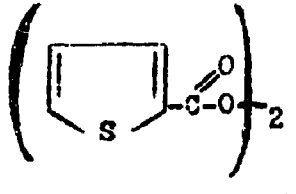
*These peroxides have been prepared by oxidation of the corresponding hydrocarbon with molecular oxygen.
**The physical constants are taken from the underlined reference.

4. PEROXIDES OF STRUCTURE RC-OO-R (PERESTERS)

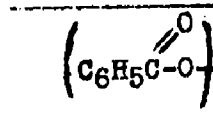
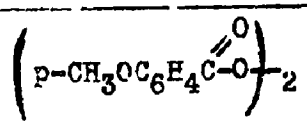
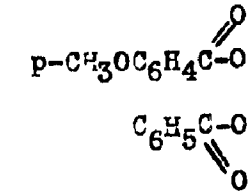
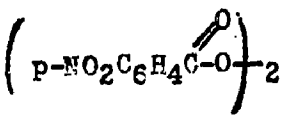
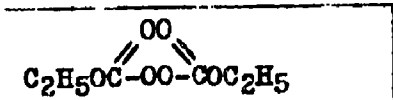
Name	Formula	Refractivity $n_D^{20°}$	Melting Point °C.	Boiling Point °C/mm.Hg.	Literature Reference*
Ethyl peracetate	$CH_3C(=O)-OOC_2H_5$ (properties not given)	——	——	——	68
Diethylperterephthalate		——	37	——	68
trans-9-Decalylperbenzoate		——	67 to 68	——	69
tert-Butyl perbenzoate	$C_6H_5C(=O)-OOC(CH_3)_3$	1.5007	——	75 to 77/2	70

*The physical constants are taken from the underlined reference.

5. PEROXIDES OF STRUCTURE $RC(=O)-OO-C(=O)R$

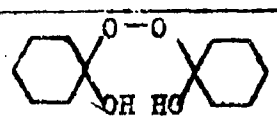
Name	Formula	Melting Point °C.	Boiling Point °C/mm.Hg.	Literature Reference*
	A. Diacyl Peroxides			
Diacetyl Peroxide	$\left(CH_3C(=O)-O-\right)_2$	30	63/21	71,72,73
Di-chloracetyl Peroxide	$\left(CH_2ClC(=O)-O-\right)_2$	36	85 (decomp.)	74
Di-n-butyryl Peroxide	$\left(CH_3CH_2CH_2C(=O)-O-\right)_2$ (Properties not given)	———	———	75
Di-phenylacetyl Peroxide	$\left(C_6H_5CH_2C(=O)-O-\right)_2$ (Properties not given)	———	———	76
Di-α-thionyl Peroxide		92 to 93(dec.)	———	77

*Physical constants are taken from the underlined reference.

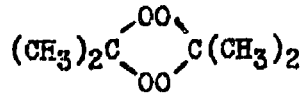
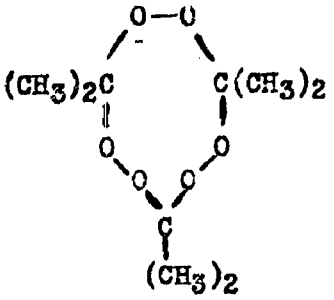
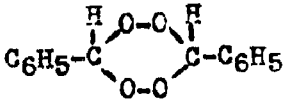
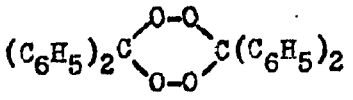
Name	Formula	Melting Point °C.	Solvent for recrystallization	Literature Reference*
	B. Diaroyl Peroxides			
Dibenzoyl Peroxide		106 to 107 (dec.)	2:1 MeOH-$CHCl_3$	78, 79
p,p'-Dimethoxybenzoyl Peroxide		129 (dec.)	Benzene	79, 80
p-Monomethoxybenzoyl Peroxide		68 to 74	3:1 Cyclohexane-Benzene	79, 81
p,p'-Dinitrobenzoyl Peroxide		158 (dec.)	Benzene	79, 82
A number of other substituted diaroyl peroxides are described in reference (79).				
	C. Dialkyl Peroxydicarbonates			
Diethyl Peroxydicarbonate		28 to 35 (dec.)	n_D^{20} = 1.4017	83
A number of other dialkyl peroxydicarbonates are described in reference (83b).				

*Physical constants are taken from the underlined reference

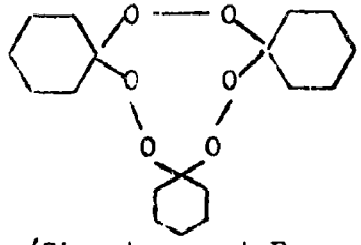
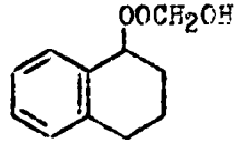
6. PEROXY DERIVATIVES OF ALDEHYDES AND KETONES

Name	Formula	Refractivity $n_D^{20°}$	Melting Point °C.	Boiling Point °C/mm.Hg.	Literature Reference**
A. Hydroxyalkyl Hydroperoxides					
Hydroxymethyl Hydroperoxide	$HOCH_2 \cdot OOH$	n_D^{16} = 1.4205	———	———	84
α-Hydroxyethyl Hydroperoxide	$CH_3CH(OH)OOH$	n_D^{24} = 1.4150	———	———	85,86
α-Hydroxyheptyl Hydroperoxide	$C_6H_{13}CH(OH)OOH$	———	40	———	85
α-Hydroxydodecyl Hydroperoxide	$C_{11}H_{23}CH(OH)OOH$	———	65 to 67	———	85,87
1-Hydroxycyclohexyl Hydroperoxide-1		———	76 to 78	———	88
B. Bishydroxyalkyl Peroxides					
bis-Hydroxymethyl Peroxide	$CH_2(OH)OOCH_2(OH)$	———	62 to 64	———	89,90
bis-Hydroxyethyl Peroxide	$CH_3CH(OH)OOCH(OH)CH_3$	n_D^{16} = 1.4265	———	———	89
Dihydroxydibenzal Peroxide	$C_6H_5CH(OH)OOCH(OH)C_6H_5$	———	———	———	91,92
bis-α-Hydroxy-β,β,β,-trichlorethyl Peroxide	$CCl_3CH(OH)OOCH(OH)CCl_3$	———	122	———	92
bis-Hydroxycyclohexyl Peroxide		———	68 to 70	———	88,93

*The physical constants are taken from the underlined reference.

Name	Formula	Refractivity $n_D^{20°}$	Melting Point °C.	Boiling Point °C/mm.Hg.	Literature Reference*
		C. Polyalkylidene Peroxides			
Dimeric Acetone Peroxide		———	132	———	93, 94, 95, 96, 97
Trimeric Acetone Peroxide	 (Structure not proven)	———	98.5	———	94, 95, 96, 97, 98
Dimeric Benzaldehyde Peroxide		———	202	———	99
Dimeric Benzophenone Peroxide		———	212.5	———	100

*The physical constants are taken from the underlined reference.

Name	Formula	Refractivity $n_D^{20°}$	Melting Point °C.	Boiling Point °C/mm.Hg.	Literature Reference*
Trimeric Cyclohexanone Peroxide	 (Structure not Proven)	———	93	———	93
	D. Monohydroxydialkyl Peroxides				
Methylhydroxy-methyl Peroxide	CH_3OOCH_2OH	$n_D^{15} = 1.3983$	——	45/17	101
Ethylhydroxy-methyl Peroxide	$C_2H_5OOCH_2OH$	$n_D^{16} = 1.4043$	——	46 to 48/13	101
Tetralylhydroxymethyl Peroxide		———	46.5	———	102
t-Butylhydroxymethyl Peroxide	$(CH_3)_3COOCH_2OH$	1.4128	——	———	103,104, 105
Methyl-α-hydroxyethyl Peroxide	$CH_3CH(OH)OOCH_3$	$n_D^{15} = 1.3930$	——	29 to 31/22	101

*The physical constants are taken from the underlined reference.

Name	Formula	Refractivity $n_D^{20°}$	Melting Point °C.	Boiling Point °C/mm.Hg.	Literature Reference*
Ethyl-α-hydroxyethyl Peroxide	$CH_3CH(OH)COOC_2H_5$	$n_D^{21.4}$=1.4021	——	50 to 52/50	101
t-Butyl-α-hydroxy-β,β,β trichlorethyl Peroxide	$(CH_3)_3COOCH(OH)CCl_3$	——	50 to 51	——	103,104, 105
E. [illegible]tals					
2,2-bis-t-Butyl-peroxypropane	$(CH_3)_3COOC(CH_3)_2OOC(CH_3)_3$	..4098	——	——	103,104, 105
bis-t-Butylperoxy phenylmethane	$(CH_3)_3COOCH(C_6H_5)OOC(CH_3)_3$	1.5770	——	——	103,104, 105
2,2-bis-t-Butyl-peroxy-4-pentane	$(CH_3)_3COOC(CH_3)(C_2H_5)OOC(CH_3)_3$	1.4200	——	——	103,104, 105
A number of other per-acetals are reported in reference (105)					

*The physical constants are taken from the underlined reference.

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